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Mikrostruktura i mikrotvrdoća odljevaka zlatnih legura

Metalographic Properties and Microhardness of Gold-Based Dental Castings

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Sažetak
Sastav i laboratorijska obradba uglavnom određuju izgled mikrostrukture te mehanička i elektrokemijska svojstva dentalnih odljevaka. **Svrha:** Svrha ovog istraživanja bila je usporediti metalografska svojstva zlatne legure s visokim udjelom zlata - Dentora S i zlatne legure s manjim udjelom zlata - Midora S. Obje se rabe u fiksnoprotetičkoj terapiji s istom indikacijom. **Materijal i metode:** Uzorci legura, modelirani u vosku, bili su odliveni centrifugalnim ljevačem u fosfatnom uložnom materijalu i ohlađeni na sobnoj temperaturi. Mikrostruktura je analizirana svjetlosnim i SEM mikroskopima. Određena je veličina zrna i udjel poroznosti u odljevcima. Izmjerena je mikrotvrdoća metodom prema Vickersu. Za statističku analizu koristio se T-test za nezavisne uzorke (α=0,05). **Rezultati:** Mikrografske snimke odljevaka obiju legura bile su različite u mikrostrukturi, homogenosti i veličini zrna. Prema ASTM-u 112/96. dokazana su znatno manja zrna u odljevku Dentora S (7,72±0,23) u odnosu prema Midoru S (6,26±0,19). Udjel poroznosti, izračunat iz površinskih onečišćenja i oštećenja, bio je znatno veći u odljevcima Dentora S (0,62%±0,24%) u odnosu prema Midoru S (0,49%±0,19%). Vrijednost mikrotvrdoće Midora S (HV0,1=169.,98±10,61) znatno je veća u odnosu prema Dentoru S (HV0,1=157,58±15,42). **Zaključak:** Može se zaključiti da sastav, uz iste laboratorijske uvjete obradbe, ima odlučujući utjecaj na izgled mikrostrukture i vrijednost mikrotvrdoće odljevka uobičajenih zlatnih legura. Odabir legure kao terapijskog sredstva, kako bi se osigurala funkcijska i tehnološka trajnost protetičkoga rada, treba se temeljiti na individualnim vrijednostima žvačnih sila pacijenta te na sastavu i mehaničkim svojstvima legure.

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Ključne riječi
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Uvod

Terapijski uspjeh u protetici ovisi- osim o anamnestičkim podacima i kliničkoj situaciji - i o dostupnosti te odabiru gradivnog materijala. Iznimno je važna i pravilna laboratorijska obradba. Na odabir legure, kao i uvijek, više utječu marketing proizvođača, ekonomski čimbenici te opremljenost dentalnog laboratorija, negoli izbor samog terapeuta.

Introduction

Therapeutic success in prosthodontics depends on several factors. There are anamnesis and clinical examination, and on the other hand, availability and selection of therapeutic materials and adequate laboratory technology. It is common that marketing influence, economic reasons, and dental laboratory's competence influence the choice of the alloy more than the therapist himself.

Mnogo je plemenitih legura za protetičku terapiju s različitim udjelom zlata kao temeljnih sastojaka (1-3). Izbor zlatne legure kao gradivnog materijala, ali i bilo koje druge, temelji se na njezinu trošenju, odnosno na individualnim vrijednostima žvačnih sila (4, 5).

Plemenite legure svojim mehaničkim svojstvima i kemijskom stabilnošću osiguravaju dugotrajnu funkciju i pozitivan terapijski učinak (1, 6-8). Većina stomatologa odabrala bi za osobnu protetičku terapiju zlatnu leguru s visokim udjelom zlata (9). No, ne može se tvrditi da su legure s visokim udjelom zlata, koje osigurava korozijsku stabilnost, najinertnije (10). Od temeljnih sastojaka u zlatnim legurama, bakar i srebro jače oksidiraju od ostalih, što čini te legure korozijski nestabilnima (11, 12). Ponašanje legure u ustima ne ovisi samo o udjelu plemenitih sastojaka, nego i o svojstvima kristalne rešetke (1, 13). Izgled mikrostrukture i sastav zrna rezultat su laboratorijskih postupaka i završne obradbe odljevka. Pritom se posebno ispituje ograničenost korištenja već lijevane kovine, utjecaj načina hlađenja i dodatne toplinske obradbe (14).

Suvremena stomatološka protetika usmjerena je na razvoj i usavršavanje novih laboratorijskih postupaka obradbe zlatnih legura, kao što je sinteriranje jedne krunice na modelu ili većih radova laserom.

Biološke danosti, primjerice promjenjivost sline kao elektrolita, prehrana, higijenske navike i sustavne bolesti te već obavljeni protetski radovi, važniji su čimbenici od sastava legure, jer utječu na elektrokemijsku stabilnost zlatnih legura (15, 16). Neravnomjerna raspodjela elemenata u zrnima uzrok je interkristalne napetosti. Poroznost odljevka uzrokuje rupičastu koroziju ili nastanak lokalnog elementa, isto tako kao i hrapava površina. Izlučivanje pojedinih rizičnih elemenata iz legure presudnije je za njezino ponašanje, negoli prisutnost tog elementa u leguri. Nehomogenost i poroznost odljevka pojačavaju eluciju iona. No, svi se ti rezultati moraju s oprezom interpretirati ako je mikrostruktura homogena i sitnozrnata.

Gradivni materijali, pa tako i dentalne legure, podliježu Zakonu o lijekovima i tako ih treba rabiti. To znači da se moraju znati sastav, indikacije i moguće popratne pojave u primjeni neke legure. Legure koje sadržavaju bakar smatraju se citotoksičnima (17, 18). One s niklom, berilijem i paladijem ubrajaju se u potencijalne alergene. Zlato kao metal često je onečišćeno drugim elementima u tragovima. No, zlatne legure rijetko se opisuju kao alergeni (19), ali

There are a great number of noble dental alloys for prosthodontics therapy having a different amount of gold (1-3). Chosen alloy has to satisfy wear resistance and the individual bite forces (4, 5).

Gold based alloys, with their mechanical and chemical properties secure functional durability and positive therapeutic result (1, 6-8). Majority of dentists would choose a high gold-based alloy for prosthetic therapy for themselves (9). However, there is no rationale to claim that the alloy, containing high percentage of gold, is inert (10). Some components of gold alloys, copper and silver, oxidize the most. It means that these alloys are not predictably anticorrosive (11, 12). Behavior of the alloy in a patient's mouth, except for chemical composition, depends on its crystal lattice (1, 13). Microstructure of castings has been the result of laboratory procedure. It includes the limitations of old gold castings, the impact of cooling procedure and additional heat treatment (14).

Contemporary prosthodontics has also been focused on development and improvement of laboratory processing such as sinteration of gold-based alloys powder on master model for one crown, or with laser for producing a bridge.

Biological factors, including electrolytic properties of saliva, nutrition and hygienic habits, systemic diseases, and the existing prosthodontics appliances, are major factors influencing the electrochemical stability of gold castings (15, 16). Irregular distribution of elements inside grains promotes residual stress along adjacent grain boundaries. Pitting corrosion is a result of porosity and surface roughness. Metal element release is more important than the presence of these elements in an alloy. Porous and non-homogeneous casting supports the ions elution. Still, we have to take all cited results cautiously, if microstructure is finegrained and homogenous.

All dental materials including alloys are subject to medical drug legislation and this has to be accepted in practice. This implies knowledge of an alloy composition, indications and possible side-effects, before its actual application in oral cavity. The alloys containing copper seem to be citotoxic (17, 18). Dental alloys, containing nickel, beryllium, and palladium have been suspected as allergens. Gold as metal is usually contaminated with different elements in traces. Allergic reaction on gold-based alloy is rare (19). Different impurities in these alloys could be possible sensible agents, too. One should also not forget super-positioning effect of some allergens.

nečistoće u njima mogu biti primarni uzrok reakcije organizma. Ne smije se zaboraviti i superponirajući učinak alergena.

U leguri je zlato u atomskom obliku. U solima za alergološko testiranje zlato je u ionskom obliku (20, 21). Zato je upitna alergenost zlatnih legura. Česta tema rasprava su soli zlata za testiranje. Pozitivan patch-test na zlato češći je kod pacijenata koji pate od popratnih pojava tijekom stomatološke terapije ili imaju lichenoidne promjene (22, 23).

Svrha ovog istraživanja bila je usporediti odljevke dviju uobičajenih zlatnih legura tipa III, kako bi se ustanovilo u kojoj mjeri sastav utječe na izgled mikrostrukture i vrijednosti mikrotvrdoće, kao dvaju najvažnijih čimbenika u odabiru legure za fiksnoprotetičku terapiju.

Materijali i postupci rada

Kao materijal za istraživanje koristile su se dvije dostupne zlatne legure - legura s visokim udjelom zlata (Dentor S, ZC, Celje, Slovenija) i legura sa smanjenim udjelom zlata (Midor S, ZC, Celje, Slovenija). Njihov deklarirani sastav prikazan je u Tablici 1.

Gold creates atomic bonds in alloys. Gold salts used for allergy testing creates ionic bonds (20, 21). Hence, allergy to gold-based alloy is questionable. Gold salts are common objects of discussion. Positive patch test for gold is more common in patients who suffer from other dental therapy side-effects or have lichenoid changes (22, 23).

The aim of this study was to compare the castings of two different, commercially gold-based dental alloys, type III, to estimate the compositions influence on microstructure and micro hardness, as the two most important factors in choosing an alloy for prosthetic therapy.

Materials and methods

Two commercially available gold-based alloys were used in the research: high-gold dental casting alloy (Dentor S, ZC, Celje, Slovenia) and low-gold dental casting alloy (Midor S, ZC, Celje, Slovenia). Compositions are shown in Table 1.

Tablica 1. Deklarirani sastav ispitanih legura (1).
Table 1 Composition of alloys according to manufacturer (1).

Maseni udio pojedinih elemenata • Composition (wt%)								Interval taljenja • Melting range	Vickersova tvrdoća • Vickers hardness HV5	Vlačna čvrstoća • Tensile strength	Istegljivost • Elongation	Granica tečenja • Yield strength
	Au	Pd	Pt	Ag	Cu	Zn	Ir			N/m^2	%	N/m^2 Rp0.2
Dentor S	75,5	1,2	4,4	11,0	6,7	1,2	-	930-955°C	165	480	20	318
Midor S	46,0	6,0	-	39,5	7,5	x*	x*	850-920°C	200	580	4	383

*-wt% of Zn and Ir were not specified by manufacturer

Iz voska za modeliranje (Modelling wax standard; DeguDent, Hanau, Njemačka) izrezano je deset pločica dimenzija 25x10x2mm - po pet za svaku leguru. Voštani uzorci uloženi su zatim u fosfatni uložni materijal (Presovest NG, ZC, Celje, Slovenija) prema uputi proizvođača. Kalupi su se jedan sat predgrijavali na 750ºC u pećnici (ZC G8, ZC, Celje, Slovenija). Uzorci su nakon toga odliveni u indukcijskom centrifugalnom ljevaču (Motorcast, Manfredi, Turin, Italija) i ohlađeni na sobnoj temperaturi prema uputi proizvođača (1). Zatim su svi ispjeskareni česticama aluminijeva oksida veličine 110 μm, u komori pjeskarice (Smalblast, Manfredi,

For each alloy five test pieces were prepared using wax patterns with the dimensions 25x10x2mm (Modelling wax standard; DeguDent GmbH, Germany) and invested in a mold ring with a phosphate-bonded investment for precious alloys (Presovest NG; ZC, Celje, Slovenia) according to the manufacturer's recommendation.

Molds have been preheated for one hour at 750°C in furnace (ZC G8; ZC, Celje, Slovenia). The alloys were induction melted and the casting was completed in a centrifugal casting machine (Motorcast; Manfredi, Torino, Italy) following the manufacturer's instructions (1). The molds were cooled at room tem-

Turin, Italija). Nakon laboratorijske obradbe uzorci su pripremljeni za metalografsku analizu. Zaliveni su bili akrilnom smolom (VariDur 20, Buehler, Lake Bluff, IL, SAD). Brušeni su na abrazivnim pločama finoće 120, 320, 600, 1000 i 4000 (CarbiMet – Silicon Carbide Abrasive Papers; Buehler, Lake Bluff, IL, SAD). Nakon toga polirani su dijamantnom pastom finoće 3 µm, na najlonskoj podlozi (lubrikant – Blue, Buehler, Lake Bluff, IL, SAD). Poliranje je završeno dijamantnom pastom ¼ µm (lubrikant –Red, Buehler, Lake Bluff, IL, SAD) na podlozi (Masterex, Buehler, Lake Bluff, IL, SAD).

Nakon poliranja uzorci su očišćeni u 98-postotnom alkoholu i osušeni na zraku. Slijedilo je jetkanje otopinom 10%KCN i 10% $(NH_4)_2S_2O_7$ u omjeru 1:1. Svi su zatim početno jetkani dvije minute, prema uputama iz tehničke literature (24, 25). Kako se u tom razdoblju dogodila prejaka površinska korozija uzoraka legure Midor S, svi su uzorci prepolirani te postupno jetkani u intervalima od 30 sekundi. Nakon toga su osušeni i promatrani svjetlosnim mikroskopom (Olympus BH-2, Tokio, Japan) dok granice zrna nisu postale sasvim vidljive. Uzorke Dentora S bilo je potrebno jetkati 120 sekundi, za razliku od Midora S – njegova je mikrostruktura bila vidljiva nakon 30 sekundi.

Mikrostruktura uzoraka analizirana je svjetlosnim mikroskopom (Olympus BH-2, Tokio, Japan). Površina je snimljena digitalnom kamerom (Olympus, Tokio, Japan) s rezolucijom od 800x600 piksela, pod istim mikroskopom, a povećanja su iznosila sto, dvjesto i petsto puta.

Površina jetkanih uzoraka pokusno je analizirana skenirajućim elektroničkim mikroskopom (SEM) (VEGA TS5136, TESCAN, Brno, Češka Republika).

Veličina zrna prema ASTM-u E112/96 izračunata je metodom kruga, promjera 50 mm prema sljedećoj formuli (26):

$G = 3,322*\log N-2,954$ i

$N=M^2*(nu+0.5*nk)/A$

$M=100$, $A=2500\ mm^2$,

G – označava veličinu zrna prema ASTM-u E112/96,
M – povećanje,
Nu – zrna unutar kruga,
Nk – zrna na krugu
A – površinu kruga.

Na svakom uzorku obavljeno je ukupno 10 mjerenja.

Udjel poroznosti određen je mikrografski. Deset snimki na različitim mjestima površine svakog

perature before divesting. The castings were sandblasted with 110µm alumina particles in a sandblasting plant (Smallblast; Manfredi, Turin, Italy).

Samples were prepared for metallographic observation. They were embedded in acrylic resin (VariDur 20; Buehler, Lake Bluff, IL, USA) and grounded with 120, 320, 600, 1000 and 4000 grit abrasive papers (CarbiMet – Silicon Carbide Abrasive Papers; Buehler, Lake Bluff, IL, USA). They were polished with diamond paste, 3 µm, on a nylon pad (lubricant – Blue; Buehler, Lake Bluff, IL, USA). The final polishing was done with diamond paste, 1/4 µm (lubricant – Red; Buehler, Lake Bluff, IL, USA) on pad (Master-tex; Buehler, Lake Bluff, IL, USA).

The samples were bathed in a 98% ethyl alcohol and dried with warm air. Samples were etched in a solution containing 10% KCN and 10% $(NH_4)_2S_2O_7$, the ratio 1/1, for metallographic observation. All the samples were etched for 2 minutes first, according to the instructions from metallographic literature (24, 25). Since the Midor S sample distinctly corroded in that period, the samples were polished again and gradually etched in 30-seconds intervals. Dried samples were submerged to the microscope analysis (Olympus BH-2, Tokyo, Japan) after each etching interval, and the etching was repeated until the grain borders were clearly visible. Finally, Dentor S samples were etched for 120 sec. and Midor S for 30 sec.

The microstructure was documented by means of light optical microscope (Olympus BH-2, Tokyo, Japan) with a CCD digital camera (Olympus, Tokyo, Japan). One hundred, two hundreds and five hundreds time magnified surface of samples were photographed at 800x600 pixels resolution.

The surfaces of etched samples were subject to scanning electron microscope (SEM) (VEGA TS5136; TESCAN, Brno, Czech Republic, Europe) analysis.

Grain size according to ASTM El12/96 was determined using the equivalent circle diameter (ECD) method with a 50-milimeter diameter (26), where:

$G = 3,322*\log N-2,954$ and

$N=M^2*(nu+0.5*nk)/A$

with $M=100$ and $A=2500mm^2$.

G - grain size according to ASTM E112/96,
M - magnification times,
nu - grains inside the circle,
nk - grains on the circle,
A - circle area.

Ten measurements have been done on each specimen.

The porosity of castings was micrographically determined. Ten micrographs of different parts on each uzorka, snimljeno je pod povećanjem od 100 puta, na rezoluciji 800x600 piksela. Da bi se zadržala izvorna kvaliteta, digitalne su snimke pohranjene u TIFF formatu bez komprimiranja. Udjel poroznosti na površini svakog odljevka izračunat je iz prosječne vrijednosti površinskih onečišćenja i oštećenja kvantitativnim postupkom analize snimaka, uz pomoć alata za analizu snimki (ImageJ 1.34n, Wayne Rasband, National institutes of Health, SAD) (Slika 1.) (27).

Mikrotvrdoća je izmjerena na istim uzorcima prema ASTM-u E92-82 (28). Za mjerenje se koristio Vickersov mjerač tvrdoće (PMT3, PMT, Moskva, Rusija) pod opterećenjem od 0,1N (HV0,1), a vrijeme dodira bilo je 5 sekundi (29). Obavljeno je bilo po 10 mjerenja na svakom uzorku. Najviša i najniža vrijednost mjerenja na svakom uzorku (za veličinu zrna, za udjel poroznosti i za Vickersovu mikrotvrdoću) nisu uzete u izračun (28).

Za statističku analizu podataka koristio se T-test za nezavisne uzorke (α=0,05) i statistički alat Statistica 7,0 (Statsoft Inc., Tulsa, SAD).

Rezultati

Slika 2. prikazuje različita povećanja mikrografske snimke odljevaka Dentora S i Midora S

Slika 3. prikazuje SEM snimke granica zrna na odljevcima Dentora S i Midora S

Prosječna veličina zrna prema ASTM-u E112/96 odljevka Dentora S (7,72±0,23) bila je znatno različita u usporedbi s Midorom S (6,26±0,19), (Tablica 2.). Za usporedbu - veličina zrna je dana i u mikrometrima. U Dentoru S prosječna veličina zrna bila je 25 μm, a u Midoru S 40 μm. Rezultati pokazuju sitnozrnatu strukturu odljevka Dentora S u odnosu prema grublje zrnatom Midoru S.

Udjel poroznosti u odljevcima Dentora S (0,62%±0,24%) bio je znatno veći nego u Midoru S (0,49%±0,19), (Tablica 2.).

Rezultati prosječne veličine zrna prema ASTM-u 112/96, udjela poroznosti i Vickersove mikrotvrdoće prikazani su na Slici 4.

specimen were photographed at 100X microscope magnification, resolution 800x600 pixels. To obtain the highest image quality, the micrographs were saved in TIFF file format without compression. Porosity percentage of the projected area of each specimen covered by impurities and defects was calculated by quantitative image analysis processing using standard image analysis technique with computer software (ImageJ 1.34n, Wayne Rasband, National institutes of Health, SAD) (Figure) (27).

The microhardness was measured according to ASTM E92-82 (28) using Vickers hardness tester (PMT3, PMT, Moscow, USSR) under 1N loading (HV0.1) and 5 second contact time (29). Ten measurements were performed on each specimen.

The highest and the lowest values for each measurement (grain size, the porosity percentage and the Vickers hardness) were not included in calculation (28).

T-test for independent samples (α=0.05) was performed using software Statistica 7.0 (Statsoft Inc., Tulsa, USA).

Results

Figure 2 shows micrographs at different magnifications of Dentor S and Midor S castings. Figure 3 shows SEM micrographs of grain boundaries of Dentor S and Midor S castings.

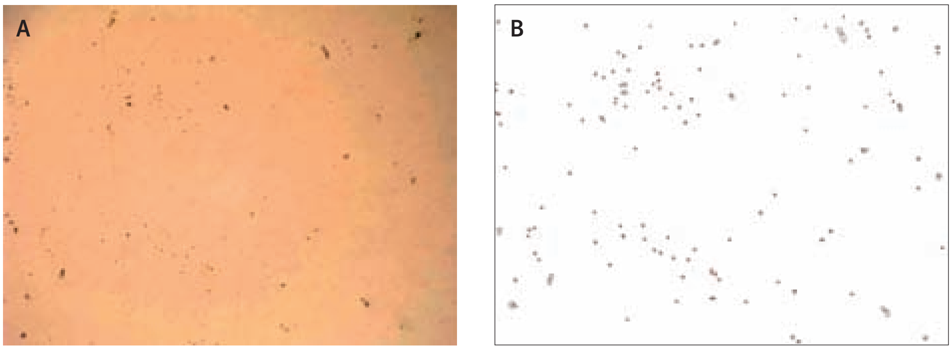
According to ASTM E112/96, the average grain size of Dentor S (7.72±0.23) castings was significantly different comparing with Midor S (6.26±0.19), (Table 2). Average grain size has also been shown in micrometers. For Dentor S 25µm and 40µm for Midor S has been obtained. Findings imply finer structure of Dentor S comparing with Midor S.

Porosity percentage of Dentor S castings (0.62%±0.24%) was significantly higher comparing with Midor S castings (0.49%±0.19%), (Table 2).

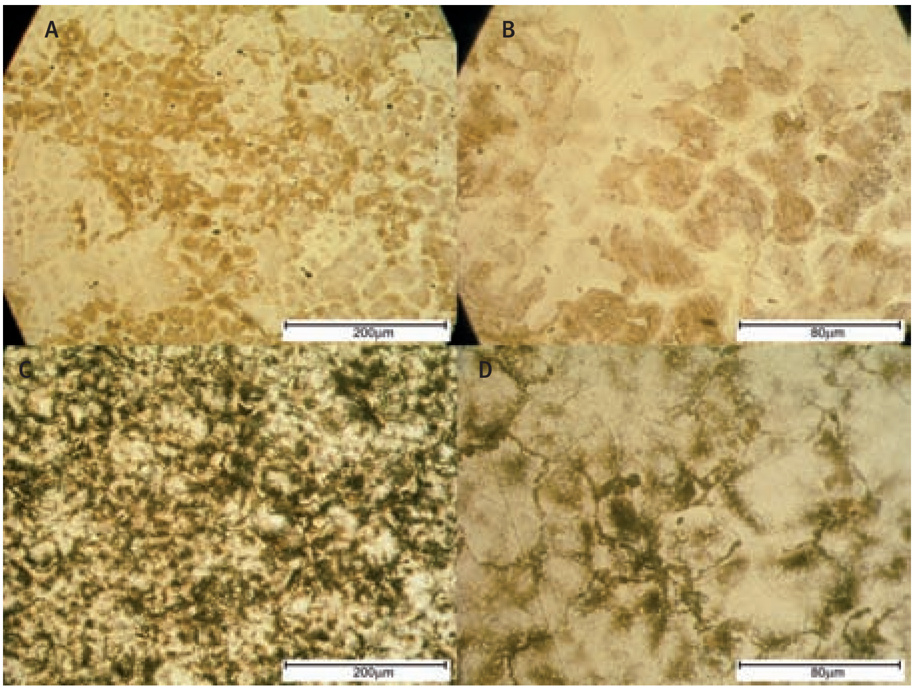
Summary results of the grain size according to ASTM112/96, the percentage porosity and the Vickers microhardness for Dentor S and Midor S are shown in Figure 4.

Tablica 2. Vrijednosti t-testa za nezavisne uzorke; za veličinu zrna, udio poroznosti i Vickersovu tvrdoću ispitivanih odljevaka.
Table 2. Values of unpaired t-test for grain size, porosity percentage and Vickers hardness of tested castings.

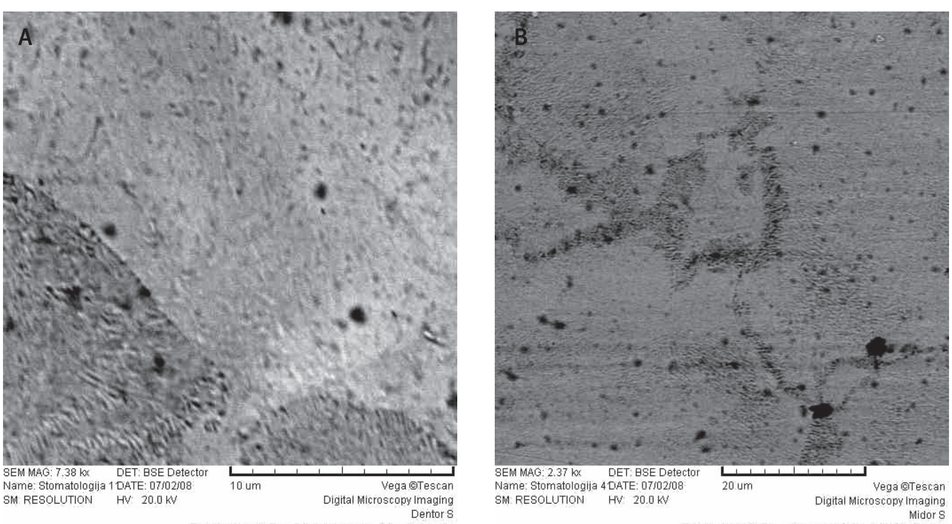
Ukupan broj mjerenja (40) • Number of measurements (40)	Dentor S		Midor S		df	SE	t-value	p<(0.05)
	Mean	SD	Mean	SD				
Veličina zrna prema ASTM 112/96 • Grain size according to ASTM 112/96	7.72 (25µm)	0.23	6.26 (40µm)	0.19	78	0.048	26.771	0.000
Udio poroznosti • Percentage porosity	0.62%	0.24%	0.49%	0.19%	78	0.0	2.677	0.009
Vickersova tvrdoća • Vickers hardness	157.58	15.43	169.98	10.61	78	2.96	4.188	0.000



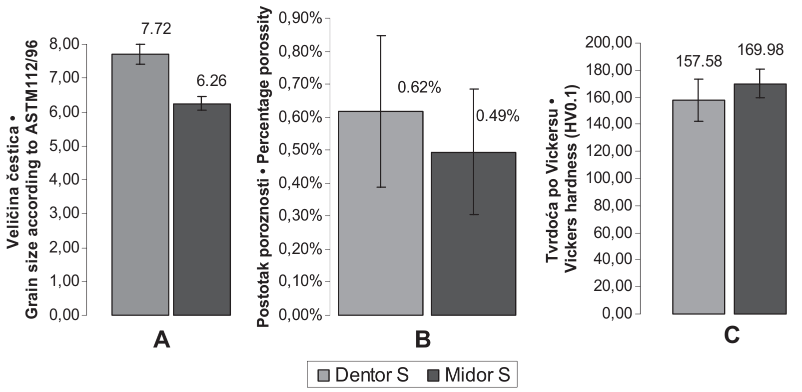
Slika 1. Mikrografska **s**nimka odljevka Dentora S (100X) s vidljivim površinskim oštećenjima i onečišćenjima (A). Izgled iste površine nakon kompjutorske obradbe snimke odljevka za određivanje udjela poroznosti (B) .
Figure 1 Light microscope micrograph (100X) of unetched Dentor S casting (A). Detected impurities and defects at same micrograph, after computer processing for percentage porosity analysis (B).



Slika 2. Mikrografske snimke pod različitim povećanjima odljevka Dentora S (A) i (B), i odljevka Midora S (C) i (D).
Figure 2 Micrographs at different magnifications of Dentor S casting (A) and (B), and Midor S casting (C) and (D).



Slika 3. SEM snimci granice zrna odljevka Dentora S (A) i odljevka Midora S (B).
Figure 3 SEM micrographs of grain boundaries in Dentor S casting (A) and Midor S (B) casting.



Slika 4. Grafički prikaz rezultata i standardne devijacije veličine zrna prema ASTM112/96 (A), udjela poroznosti (B) i Vickersove mikrotvrdoće (C)

Figure 4 Graphs and standard deviation of grain size according to ASTM112/96 (A), percentage porosity (B) and Vickers microhardness (C)

Prosječne vrijednosti mikrotvrdoće, prema Vickersu, pokazuju da su odljevci Midora S tvrđi (HV0,1 = 169,98±10,61) od odljevaka Dentora S (HV,1 = 157,58±15,42), (Tablica 2.).

Rasprava

Zlatne legure, s obzirom na broj sastojaka, u pravilu su višefazne (1, 30). Svaka svojim većim ili manjim udjelom pridonosi optimizaciji mehaničkih i elektrokemijskih svojstava odljevaka. Zlato štiti od korozije, pridonosi istezljivosti, ali i povećava specifičnu težinu legure. Istodobno se pokazalo da smanjeni udjel zlata u sastavu čini leguru osjetljivijom na tehničke pogreške, a time i na laboratorijsku obradbu. Prve zlatne legure sadržavale su maseni udjel od 8 do 20 posto bakra, kako bi se snizili intervali taljenja i omogućilo otvrdnuće (1-3, 13). U objema ispitivanim legurama, deklarirani maseni udjel bakra je manji od 10 posto. Maseni udjel srebra u objema legurama je u dopuštenom udjelu od 42 posto. Tako velik udjel srebra u leguri Midor S zamjenjuje određeni maseni postotak zlata, kako bi se dobila ekonomična legura za iste terapijske indikacije. Naime, srebro sa zlatom stvara čvrst rastvor u svim težinskim omjerima. Omjer sebra i bakra mora se pažljivo odrediti, jer nisu međusobno topljivi. Dodatkom drugih plemenitih metala, kao što su paladij ili platina, želi se povećati mikrotvrdoća i smanjiti veličina zrna odljevka.

Platina u leguri s visokim udjelom zlata, kao što je Dentor S, povećava mehanička svojstva bolje nego bakar. Istodobno, reagirajući s bakrom, platina sudjeluje u precipitacijskom otvrdnuću. Zbog razmjerno visokog tališta u odnosu prema zlatu, maksimalni maseni udjel platine ne prelazi 3 do 5 posto.

Paladij gradi čvrste otopine sa zlatom, srebrom i bakrom. U ispitivanim legurama udjel paladija nije bio veći od dopuštenog masenog udjela od 8 posto. Paladij je bio znatno jeftiniji u doba kada su se te legure pojavile na tržištu. Lakši je od platine, pridonosi

Midor S castings (HV0.1 = 169.98±10.61) were significantly harder than Dentor S castings (HV0.1 = 157.58±15.42), (Table 2).

Discussion

Gold-based alloys are multiphase because they contain different elements with different chemical affinity (1, 30). Each element has to improve mechanical and/or electrochemical properties. Gold protects from corrosion, enlarges elongation, but also increases the density of an alloy. Lower percentage of gold generally makes alloys more sensitive to technical errors and laboratory treatment. First gold-based alloys contained 8-20 wt% of Cu to increase their melting temperature and to impart age hardening (1-3, 13).

In both tested alloys, amount of copper was less than 10 wt% and silver was below the allowed 42 wt% limit. Great amount of silver in Midor S alloy has been added to substitute a certain portion of gold and bring cheaper alloy for the same indication. Silver and gold form solid solutions in all proportions. The ratio of silver and copper must be carefully balanced in low gold alloys because silver and copper are not miscible. Addition of other noble metals, like palladium and platinum, have increased hardness and decreased the grain size of gold-based castings.

Platinum in high gold-based alloy like Dentor S, improves mechanical properties even better than copper. In reaction with copper, it takes part in age hardening. Because of its very high melting point comparing with gold, maximum content of platinum averages 3-5 wt%.

Palladium creates solid solutions with gold, silver and copper. In tested alloys it doesn't reach its limit of 8%. Palladium was much cheaper in the period when gold-palladium based alloys were introduced tvrdoći i čvrstoći legura te smanjuje otpuštanje bakra iz odljevaka. Zbog visokog tališta dodaje se zlatnim legurama radi povišenja likvidus-temperature u intervalu taljenja, povećava broj nukleacijskih mjesta i istodobno omogućuje smanjenje udjela zlata povećanjem udjela srebra (1, 10). No paladij, zbog osjetljivosti na sumpor i njegove spojeve, može uzrokovati krtost odljevka.

Izmjerena veličina zrna manja je u uzorcima Dentora S (25μm) negoli u Midoru S (40 μm). Sedej i Kuliš (8) su dokazali da, ako se doda iridij u eksperimentalnu leguru Midora S, nastaje sitnozrnatiji odljevak u odnosu prema istovjetnoj leguri bez iridija. Veličina zrna smanjena je s 400 do 420 μm na 40 μm. Izmjerene vrijednosti veličine zrna od 40 μm uzorka Midora S u ovom ispitivanju odgovaraju rezultatima Sedeja i Kuliša (8) te onima Bessinga i Bergmana (31) za zlatne legure tipa III. Nielsen i Tucillo (32) dokazali su da manji udjel iridija ili rutenija, dodan zlatnoj leguri, povećava broj centara i brzinu nukleacije, te se tako smanjuje veličina zrna u odljevku. Općenito, većina proizvođača suvremenih legura koristi se primjesama za proizvodnju legure sitnijeg zrna. Mehanička svojstva, kao što su vlačna čvrstoća i istezljivost, znatno su bolja ako se postigne struktura sitnijeg zrna. Na tvrdoću i granicu tečenja struktura sitnijeg zrna ima znatno manji učinak (33).

Mikrotvrdoća je jedno od najvažnijih mehaničkih svojstava legure. Izmjerene vrijednosti znatno su veće za odljevke Midora S, vjerojatno zbog većeg udjela paladija i srebra negoli u Dentoru S. Obje ispitane legure - Dentor S i Midor S - zadovoljavaju ADA-ov standard za zlatne legure tipa III (34). Opravdanost primjene obiju legura za teleskopske sustave istraživao je Šušulić (35, 36), uspoređujući ih s drugim uobičajenim legurama s visokim i niskim udjelom zlata. U laboratorijskim uvjetima obje su bile otporne na frikcijsko trošenje i imale su zadovoljavajuću retenciju.

Da Silva i Muench (37) dokazali su da vrijednosti mehaničkih svojstava, kao što su tvrdoća i vlačna čvrstoća zlatnih legura s niskim udjelom zlata, rastu s precipitacijskim otvrdnućem. Naime, nakon lijevanja i homogenizacijskog žarenja odljevci su mekši i istezljiviji, što ograničava primjenu te vrste legure za protetske radove većih raspona.

Adekvatna laboratorijska obradba znatno pridonosi ciljanim svojstvima odljevka. Odlijevanje u nepregrijani uložni materijal smanjuje reaktivnost taline. Pritom je povećan broj centara nukleacije, što sprječava rast zrna. Ako se naglo hladi, dobit ćemo nehomogen odljevak sitnog zrna. Taljenje otvore-

on the market. It is less dense than platinum, it increases hardness and strength of gold alloy, and decreases copper release from castings. Because of its high melting point, palladium increases melting interval of an alloy, promotes nucleation and permits reducing the percentage of gold in alloys and increasing the content of silver. Added to low-gold alloys, it prevents tarnish and corrosion, also has a whitening effect even when used at a low concentration (1, 10). However, palladium is sensitive to sulphur and its compounds which makes castings more brittle.

Smaller grains were measured in Dentor S castings (25μm) comparing with Midor S (40μm). Sedej and Kuliš (8) observed that addition of iridium in the experimental alloy Midor S brought finer structure of castings. Grain size was decreased from 400-420μm to 40μm. Obtained values of grain size in Midor S (40μm) corresponds with results reported by Sedej and Kuliš (8) as well as with results from Bessing and Bergman (31) in case of low-gold-based alloys type III.

Nielsen and Tuccilo (32) have proved that traces of iridium and ruthenium added to gold-based alloy promote and accelerate nucleation, and decrease the grain size. Generally, most alloy manufacturers use grain refinement in present-day products. The tensile strength and elongation have been improved significantly by the fine grain structure. However, the grain refinement showed less effect on hardness and yield strength (33).

The microhardness represents one of the most important mechanical properties of castings. Obtained values were significantly higher for Midor S castings, because of greater palladium and silver amount. Tested alloys, Dentor S and Midor S, satisfy the ADA standard for gold alloys, type III (34). Šušulić (35, 36) tested both alloys for telescope system comparing them with other commercial high and low gold-based alloy. In laboratory condition, both alloys satisfied wear resistance and retention ability. Da Silva and Muench (37) found that mechanical properties of low gold-based alloy, like tensile strength and proportional limit, were high when precipitated. After heat treatment, including casting procedure and homogenization, castings had lower yield stress and increased ductility, which is not appropriate for long span bridges.

Optimal laboratory procedure can crucially contribute to adequate properties of castings. Casting in a cold mold reduces reactivity of castings. Nucleation is increased and grains growth slow down. Rapid cooling promotes nonhomogeneous but fine-grained nim plamenom usitnjuje zrno zbog moguće redukcije i oksidacije taline plamenom i utjecajem atmosfere, ali istodobno stvara opasnost od poroznosti i krhkosti odljevka (11,38).

Mikrostruktura uzoraka Dentora S gotovo je dendritska. Na nekim mjestima vide se segregacije različitih faza. Brojenje zrna metodom kruga upućuje na strukturu sitnijeg zrna. U odljevcima Midora S zrna su veća i njihove granice nisu potpuno jasne te ih je teško odrediti.

Osim toga vidljiva je tamna faza, što dodatno otežava analizu. Radi se o izmiješanim kristalima s različitom zastupljenosti atoma pojedinih sastojaka u njima, što govori u prilog nehomogenoj strukturi. Sama struktura tijekom jetkanja određuje svojstva legure. Upravo različitost sastava faza uvjetovala je različito vrijeme jetkanja uzoraka, a očituje se u neravnoj površini uzorka.

Preliminarne SEM-snimke kod različitih povećanja pokazuju granice zrna Dentora S i Midora S. Vidljiva je dendritičnost Dentora S, a same granice zrna su oštre i prepoznatljive (Slika 2.A). Granice zrna Midora S porozne su (Slika 2.B) zbog onečišćenja te oksida i to su prva korozijski aktivna mjesta tijekom jetkanja (33). Bessing i Bergman (31) te Hero sa suradnicima (39) pokazali su da su segregacije unutar zrna i na granicama zrna znatno veće kod zlatnih legura sa smanjenim udjelom zlata prema zlatnim legurama tipa III. Zbog te nehomogenosti bilo im je znatno teže odrediti njihove granice.

Sedej i njegovi kolege (40) metalografski su i uzorkovanjem dokazali da površinsko tamnjenje različitih odljevaka zlatnih legura nastaje zbog reakcije površinskog srebra i sulfida iz sline. Obojenje je češće kod nehomogenih odljevaka, jer ioni srebra lakše putuju prema površini. Autori smatraju da srebro uzrokuje dendritsku kristalizaciju, ako se legura pregrije ili ne obavi naknadna toplinska obradba.

U praksi se plemenite legure često ponovno lijevaju. Horasawa i Marek (41) su u ponovnom lijevanju srebrnih legura dokazali rast zrna i porast mikrotvrdoće. Kod petog lijevanja nastala je substruktura unutar zrna i smanjio se površinski udjel zlata. Ukupna koncentracija Au, Ag i Pd bila je nepromijenjena, a količina bakra i cinka smanjivala se tijekom svakog novog lijevanja. U petom lijevanju znatno su bila smanjena potrebna svojstva odljevka, što upućuje na ograničenost ponovljenog lijevanja. Tijekom skrućivanja taline ioni bakra i cinka reagiraju s kisikom te nastali oksidi putuju na površinu odljevka. Završnom površinskom obradbom - poliranjem i pjeskarenjem, oni se uklanjaju s površine

structure of castings. Melting with open flame also brings finer grains because of oxidation and reduction of a melting alloy by gas and atmosphere. This also takes porosity and brittleness of casting (11, 38).

The microstructure of Dentor S castings is almost dendritic. In some places, there are segregations of certain phases. The measurement and determination of grain size using the ECD method indicate that grains are finer. Grains in Midor S castings are greater and borders are not clearly apparent. There is a certain dark phase, because of reaction to etching solution, which makes the analysis more difficult. Observed castings are nonhomogeneous, a multiple-phase with irregular polycrystalline grains, because some elements are not soluble in one another. In addition, phase structure affects etching characteristics of alloy. Since each phase was etched at a different rate, etching creates a rough surface.

Preliminary SEM micrographs at diverse magnifications show grain boundaries of Dentor S and Midor S. The dendrites of Dentor S are more visible and boundaries are sharper and clearer (Figure 2A). Grain boundaries of Midor S are more porous (Figure 2B) because there are more impurities and oxides and they are a site of first corrosive attack by etching (33). Bessing and Bergman (31) and Hero et al. (39) found larger interdendritic and boundary segregations in low gold alloys than in type III gold alloys. It was more difficult to determine the proper grain size because of such inhomogeneities.

Sedej et al. (40) also found by metallographic methods and electroprobe analysis that surface tarnish of different gold castings was caused by the chemical reaction between silver at the surface of castings and sulphides from saliva. Coloration was more frequent in inhomogeneous castings due to the remarked segregation and flow of silver at the surface of castings. Authors suggest that silver promotes dendritic crystallisation if alloy was heated over the melting temperature range and if moulds were not afterwards heat treated.

In practice, noble and semi-noble dental casting alloys are often reused by recasting. Horasawa and Marek (41) found increasing of hardness and grain growth in tested silver based dental alloy after recasting of alloys. They found increased sub-grain formation after the fifth recasting, too. The elemental map showed decreased surface concentration of Au during the fifth casting. The bulk concentrations of Au, Ag and Pd remained constant, but the copper and zinc contents slightly decreased after each recasting. A severe degradation of properties was obprotetskoga rada. Ponovljenim lijevanjem iste legure jako se povećava udjel uključevina i nečistoća. Reisbick i Brantley (42) istaknuli su da ukupan broj oštećenja raste sa svakim ponovljenim lijevanjem i uzrokuju produljenje do loma radova od zlatnih legura sa smanjenim udjelom zlata. Marx (43) je pokazao da se ponovnim lijevanjem zlatno-paladijevih legura smanjuju vrijednosti mikrotvrdoće i vlačne čvrstoće. Gubitak tih svojstava smanjit će se indukcijskim taljenjem i dodatkom barem jedne trećine nove legure.

Poboljšanje mehaničkih svojstava odljevka postiže se određenim postupcima prije i poslije lijevanja (1, 14, 44). Tvrdoća zlatnih legura sa sniženim udjelom zlata može se povećati kaljenjem, ili jednim od mehanizama očvrsnuća, na primjer stvaranjem intermetalnih spojeva, Au-Cu i Cu-Pd. Kim i suradnici (45) smatraju da otvrdnuće komercijalnih zlatnih legura tipa III nastaje tijekom AuCu1' faze unutar zrna. Otvrdnuće ovisi o sastavu sekundarne faze te njezinoj rasprostranjenosti kroz ostale faze (33). Hero i suradnici (39) istraživali su strukturu i koncentracijski gradijent odljevaka konvencionalnih zlatnih legura tipa III i zlatnih legura sa sniženim udjelom zlata. Kod legura sa sniženim udjelom zlata dokazali su veću prisutnost lamelarne eutektične faze na rubovima zrna, ali i lamelarnu građu unutar zrna, što je rezultat nastanka Au-Ag i Au-Cu spojeva kao posljedice kemijske sklonosti na povišenim temperaturama. Međusobna sklonost pojedinih elemenata može se potaknuti i drugim elementima u leguri, posebice bakrom. Ako se postignu isti laboratorijski uvjeti i obavi toplinska obradba prema uputi proizvođača, minimalna su odstupanja u veličini zrna kod zlatnih legura s visokim udjelom zlata (1-3, 10).

Zlato, paladij i platina kemijski su stabilni te je minimalna elucija njihovih iona u usnoj šupljini (46). Višefazni odljevci otpuštaju više iona od jednofaznih. Liden je dokazao otpuštanje metala iz nakita s različitim udjelom zlata u otopinu umjetnog znoja. Kemijskom analizom, induktivnom spregnutom plazmom (ICP-om) i atomskom adsorpcijskom spektrometrijom (AAS-om), nije dokazao otpuštanje iona zlata (7). Sve to govori u prilog elektrokemijskoj stabilnosti zlatnih legura, što je uvjet za izostanak sustavnih reakcija organizma na protetičke radove od zlatnih legura.

served after the fifth cast. The results indicate that these dental alloys can be safely recast only a small number of times. During grain formation copper and tin ions react with different oxides and escape on the surface of casting. These surface oxides were moved away by polishing and sandblasting.

Inclusions and impurities rapidly grow in multiple cast noble alloys. Reisbick and Brantley (42) revealed that the number of casting defects increased with re-melting, and that their presence dominates the tensile fracture process in low gold-based alloy. Marx (43) found that the recasting of gold-platinum alloy decreases hardness and tensile strength. Decrease was lower if an alloy melted electrically and if at least one third of new alloy was added. Improvement of mechanical properties of castings is possible by additional heat treatment (1, 14, 44).

Hardness of low gold-based alloys can be increased by annealing or by creating inter-metal Au-Cu and Cu-Pd compounds. Kim et al. (45) found that the hardening in a commercial type III could be attributed to the formation of the metastable AuCu 1' type ordered phase in the grain interior. Strengthening depends on the composition of the second phase and dispersion throughout the other phases (33). Hero et al. (39) observed the structure and concentration gradients in the as-cast state of a low gold-based alloy and a conventional type III gold-based alloy. A much more lamellar eutectic phase was found at the grain boundaries in the low-gold-based alloy. They showed that the interior of the grains consisted of fine lamellae, as result of formation of Au-Ag and Au-Cu rich bands due to the chemical liability at high temperatures. Obviously, higher affinity of some elements can be induced by other elements, especially by copper. Under the same laboratory conditions and strict heat treatment following detailed instructions, changes of grain size in high gold-based alloys are minimal (1-3, 10).

Gold, palladium and platinum have superior chemical stability and are unlikely to be released at high levels in the mouth (46). Multi-phase castings may release more ions then single-phase. Liden studied metal release from different gold-containing jewelry stored in artificial perspiration. For chemical analysis, inductively coupled plasma detection (ICP) and atomic absorption spectrophotometry (AAS), with flame and with furnace, were used. No release of gold was detected (7). This indicates that gold-based alloys are electrochemically stable, which is a prerequisite for the absence of systemic reaction of organism on gold-based castings.

Zaključak

Liječnik je odgovoran za provedenu protetičku terapiju. To znači da mora poznavati sastav i svojstva lijevane legure nakon laboratorijske obradbe, a prije inkorporacije u usta pacijenta. Ispitane zlatne legure imaju različit sastav, posebice u udjelu zlata, srebra i paladija. Analizirajući mikrostrukturu, odljevci legure s većim udjelom zlata homogeniji su, sitnozrnatiji, ali manje mikrotvrdoće negoli legura sa smanjenim udjelom zlata. Statistički znatno veća mikrotvrdoća legure sa smanjenim udjelom zlata rezultat je većeg udjela srebra i paladija negoli u plemenitijoj leguri. Dokazani veći udjel poroznosti kod Dentora S može smanjiti očekivanu korozijsku stabilnost te legure.

Može se zaključiti da će legura sa sniženim udjelom zlata, koje je nadomješteno povećanim udjelom srebra i paladija, vjerojatno zadovoljiti žvačnu funkciju zbog većih vrijednosti mikrotvrdoće. No, ako želimo zadovoljiti terapijski učinak te korozijsku stabilnost i mehaničku otpornost, to zahtijeva homogenizacijsko i precipitacijsko žarenje odljevaka obiju legura.

Zahvale

Objavu rada pomoglo je Ministarstvo znanosti, obrazovanja i športa.

Conclusion

The dentist is responsible for the conducted prosthetic therapy. That implies the knowledge of composition and properties of an alloy after laboratory procedure, but before its incorporation in patients mouth. Analyzed gold-based alloys have different composition, especially of silver, gold and palladium. The microstructure of high gold castings was more homogeneous with finer grains, but lower microhardness. The higher microhardness of low gold-based alloy is a result of greater silver and palladium amount as well as non- homogeneous microstructure. Significantly higher percentage of porosity in Dentor S could contribute to lower corrosion resistance, although the etching time speaks about corrosion stability indeed.

It could be concluded that the low gold-based alloy with greater contents of silver and palladium would satisfy more likely masticatory function because of greater microhardness values. However, to satisfy therapeutic success meaning corrosion stability and mechanical resistance, heat treatment of both castings has to be done.

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Abstract

Composition and laboratory procedures have the greatest influence on the microstructure, mechanical, and electrochemical properties of dental casts. **Objectives:** The aim of this study was to evaluate the metallographic properties of high gold-based dental castings, Dentor S, and low gold-based dental castings, Midor S, used for the same fixed prostehtic indication. **Material and methods:** Samples were centrifugally cast in a phosphate-bonded investment and cooled at room temperature. The microstructure was analyzed and photographed with light microscope and scanning electron microscope. The grain size and the percentage porosity were evaluated. The Vickers microhardness was tested. T-test for independent samples (α=0.05) was used for statistical analysis. **Results:** Micrographs showed difference in microstructure, homogeneity and grain size. Average grain size number according to ASTM112/96 of Dentor S (7.72±0.23) was significantly greater comparing with Midor S (6.26±0.19) castings. Percentage porosity of castings was calculated from average impurities and defects, where Dentor S (0.62%±0,24%) was significantly more porous than Midor S (0.49%±0.19%). Vickers microhardness of Midor S castings (HV0.1=169.98±10.61) was significantly greater then those of Dentor S castings (HV0.1=157.58±15.42). **Conclusion:** It can be concluded that composition, under the same laboratory procedures, has a critical influence on microstructure and microhardness of conventional gold-based castings. To ensure functional and technical durability of restoration, selection of the alloy should be based on its composition and mechanical properties as on the patient's bite forces.

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